1st Interim Report, Contract No. N68171-95-C-9105

Title: Isodisperse Telechelic Polymers and their Polyurethane Derivatives. Sample preparation.

In the first part of the Contract, three HTPBD samples have been prepared, characterized by the following molecular weights:

No. 1. Nominal: $\overline{M}_n = 3000$
Experimental: $\overline{M}_n = 3250$
Polydispersity: $\overline{M}_w/\overline{M}_n = 6460/3250 = 1.98$

No. 2. Nominal: $\overline{M}_n = 2000$
Experimental: $\overline{M}_n = 1870$
Polydispersity: $\overline{M}_w/\overline{M}_n = 3030/1870 = 1.62$

No. 3. Nominal: $\overline{M}_n = 5000$
Experimental: $\overline{M}_n = 5230$
Polydispersity: $\overline{M}_w/\overline{M}_n = 9022/5260 = 1.72$

Although the polydispersities of the samples are slightly different, they are within the limits given in our US Patent ($\overline{M}_w/\overline{M}_n = 1.5$ to 2.0). Due to the different molecular weights, every sample was prepared with a somewhat different polymerization recipe, the details were given in our previous 1st Interim Report (September 28, 1995, Contract No. N68171-95-C-9086). The No. 1. sample was handed personally by Prof. F. Tüdős to dr. G. Hagnauer on July 6, this year, in Watertown. The No. 2. and No. 3. samples were sent by air mail on October 13, this year. The structures of the samples were characterized by FT-IR, ^{1}H-NMR and GPC investigations. The measurements are given graphically, their evaluations are summarized in the Table 1.

The ^{1}H-NMR spectra of the samples were recorded by a Varian 400 type instrument.

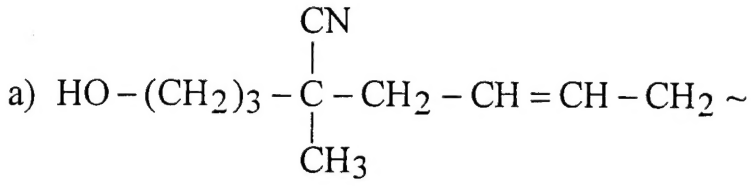
Figures 2-4 show the ^{1}H-NMR spectra of the samples HTPBD-2000, HTPBD-3000 and HTPBD-5000. All the three spectra consist of three regions. The aliphatic -C$\underline{H}_2$-CH=CH-CH_2 and -CH=CH-C$\underline{H}_2$-C$\underline{H}_3$ protons appear at 1.0-2.2 ppm. The peaks appearing in the range 3.7-4.1 ppm correspond to the protons of -C$\underline{H}_2$- and -C$\underline{H}$ groups adjacent to the chain-end -OH groups. The peaks characteristic to protons of unsaturated -C$\underline{H}$=CH- and -C$\underline{H}$=C- groups formed from 1,4 and 1,2 linkages in the repeating units of polybutadiene appear at 4.9-5.5 ppm. The ratio of integrals of the peaks belonging to the protons of these both groups gives the ratio of butadiene units built in to the polymers with 1,2 and 1,4 linkages. According to the calculations, one 1,2 linkage falls to about five 1,4 linkages (see Table 1.).

Table 1. Microstrucure of HTPBD samples based on FT-IR and ^{1}H-NMR measurements

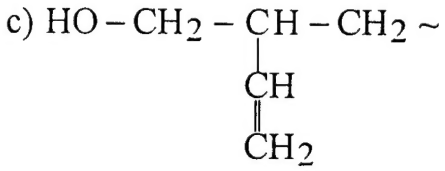
Sample	Microstructure by					
	FT-IR (Fig.1.)			^{1}H-NMR		
	1,2 bond	1,4 bond cis	1,4 bond trans	1,2 bond	1,4 bond	Figure, HTPBD-
	%			%		
1	13	53	34	17.8	82.2	-3000
2	13	54	33	16.6	83.4	-2000
3	13	54	33	16.9	83.1	-5000

Owing to the combined initiation and to the combination of 1,2- and 1,4- units formed during chain propagation, the NMR can distinguish three OH structures at the chain-end:

Chemical shift:

a)  3.71 ppm

b) HO-CH_2-CH=CH-CH_2~ 4.08 ppm

c)  4.42 ppm

Molecular weight distribution was estimated by gel permeation chromatography (GPC) method using Waters basic equipment: pump model 510, injector model U6K and a set of four chromatographic columns packed with crosslinked polystyrene gel, ("ultrastyragel") of particle size less than 10 microns and pore size of 10E3, 10E2, 100 and 50nm. The molecular weight distributions are given graphically.

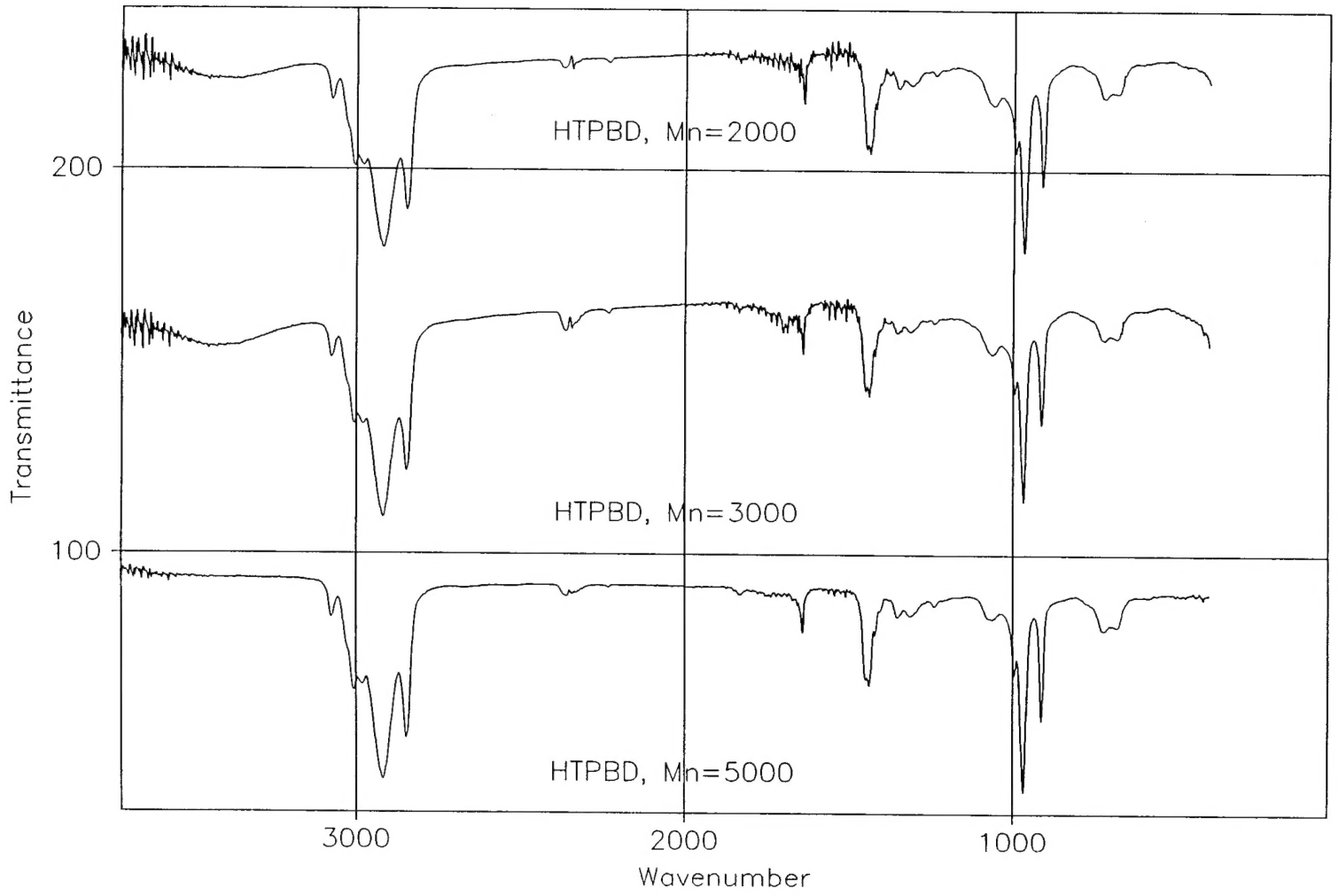
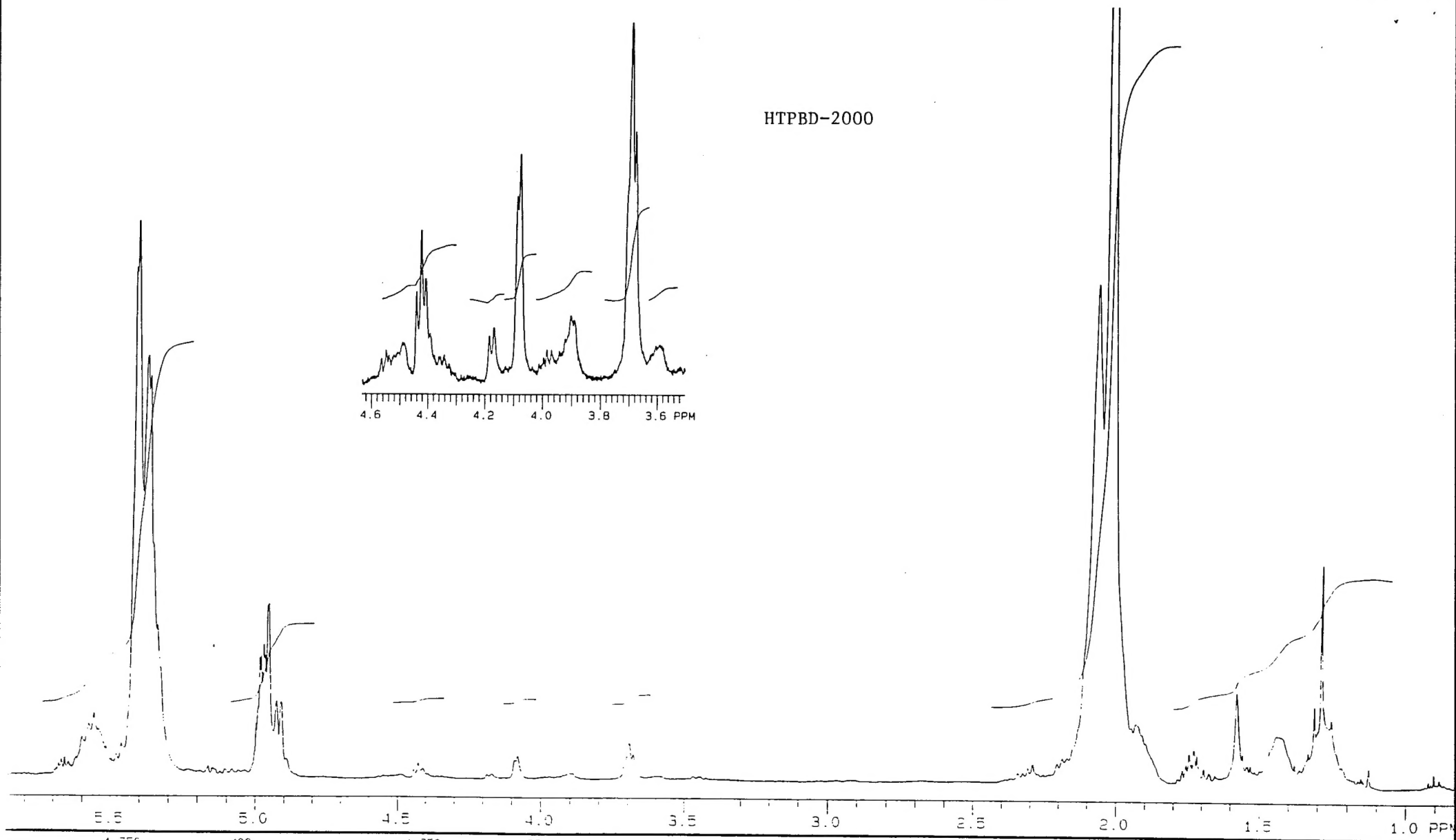


Figure 1. FT-IR spectra of polybutadiene diol samples.

HTPBD-2000



Nucleus 1.750	Freq 400 MHz	Nucleus 1.750	Offset 75.0 Hz
Spec Width 5000.0 Hz	Offset 327.0 Hz	Mode NNN	Power 20 db
Acq Time 3.974 sec	Delay 0 sec	Modulation Mode C	Freq 200 Hz
Pulse Width 7.0 µsec	Transients 16	Pulse Width ___ µsec	Power Mode ---

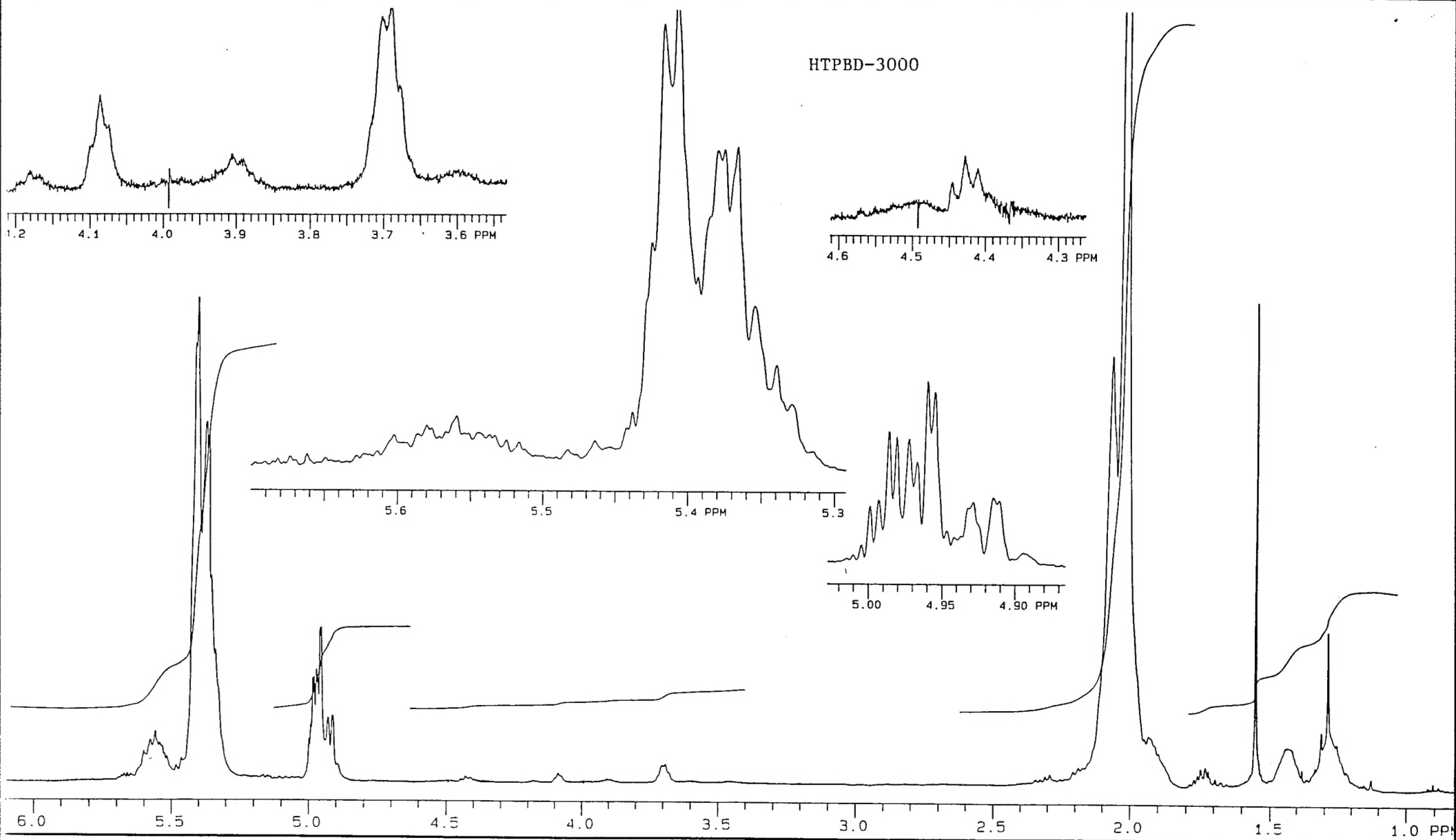
FN 32	RE --- sec	CD --- sec
LB --- Hz	AF --- sec	CCD ---
Width 3040.3 Hz ppm	Start 319.8 Hz/ppm	
Reference		

Pulse Sequence STD1H	
Tube OD ___ mm	
Temp --- °C	
Solvent CDCL3	

SAMPLE
H-7378 (18600)
POLIBUTADIEN (CDCL3) PBu-121
KESZLER B./E.O.

Number ___
File HBE162
Date 13-09-95
XL VXR 400 VS

HTPBD-3000

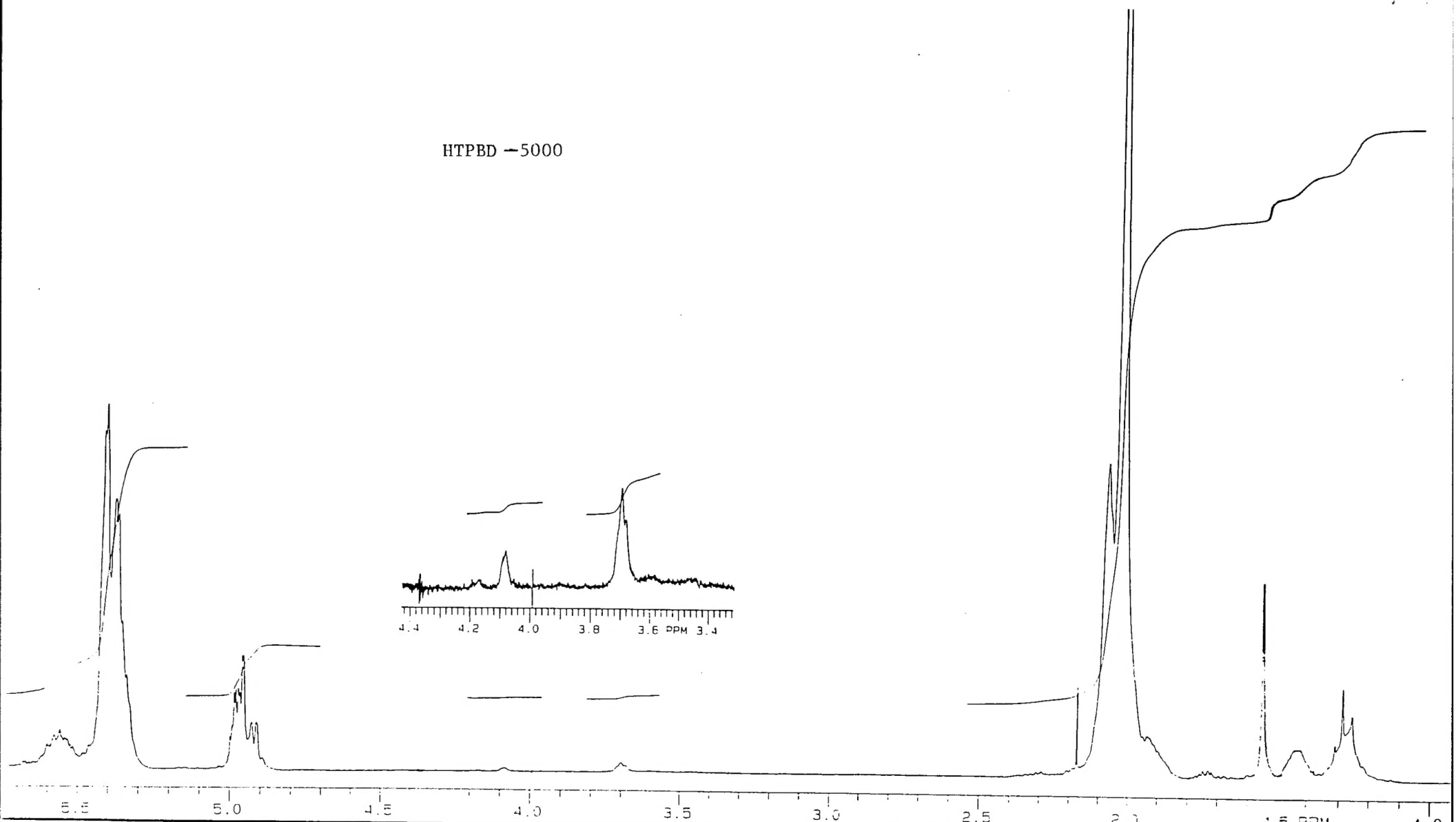


ACQUISITION				DECOUPLE				PLOT/PROCESSING				EXPERIMENT			
Nucleus	1.750	Freq	400 MHz	Nucleus	1.750	Offset	75.0 Hz	FN	32	K RE	--- sec	CD	--- sec	Pulse Sequence	STD1H
Spec Width	4000.0 Hz	Offset	-174.8 Hz	Mode	NNN	Power	20 db	LB	--- Hz	AF	--- sec	CCD	---	Tube OD	--- mm
Acq Time	4.000 sec	Delay	0 sec	Modulation Mode	C	Freq	200 Hz	Width	2139.0 Hz/ppm			Start	308.1 Hz/ppm	Temp	--- °C
Pulse Width	7.0 µsec	Transients	32	Pulse Width	--- µsec	Power Mode	---	Reference						Solvent	CDCL3

SAMPLE
H-7096 (18382)
118 (CDCL3)
KESZLER B./III.11.
PROTON SURVEY/G.E.

Number
File H
Date 21-06-95
XL VXR 400

HTPBD —5000



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Spec Width 5000.0 Hz	Offset -174.8 Hz	Mode NNN	Power 20 db	LB --- Hz	AF --- sec	CCD ---	Tube OD mm	PBU-126 (CDCL3)	File K226H
Acq Time 4.000 sec	Delay 0 sec	Modulation Mode C	Freq 200 Hz	Width 1947.1 Hz/ppm	Start 372.3 Hz/ppm		Temp ---°C	KESZLER B./E.O.	Date 14-09-95
Pulse Width 7.0 μsec	Transients 16	Pulse Width μsec	Power Mode ---	Reference			Solvent CDCL3		XL VXR 400

VISCOTEK CORP. UCAL 4.05 ENDED: 06/14/95 13:52
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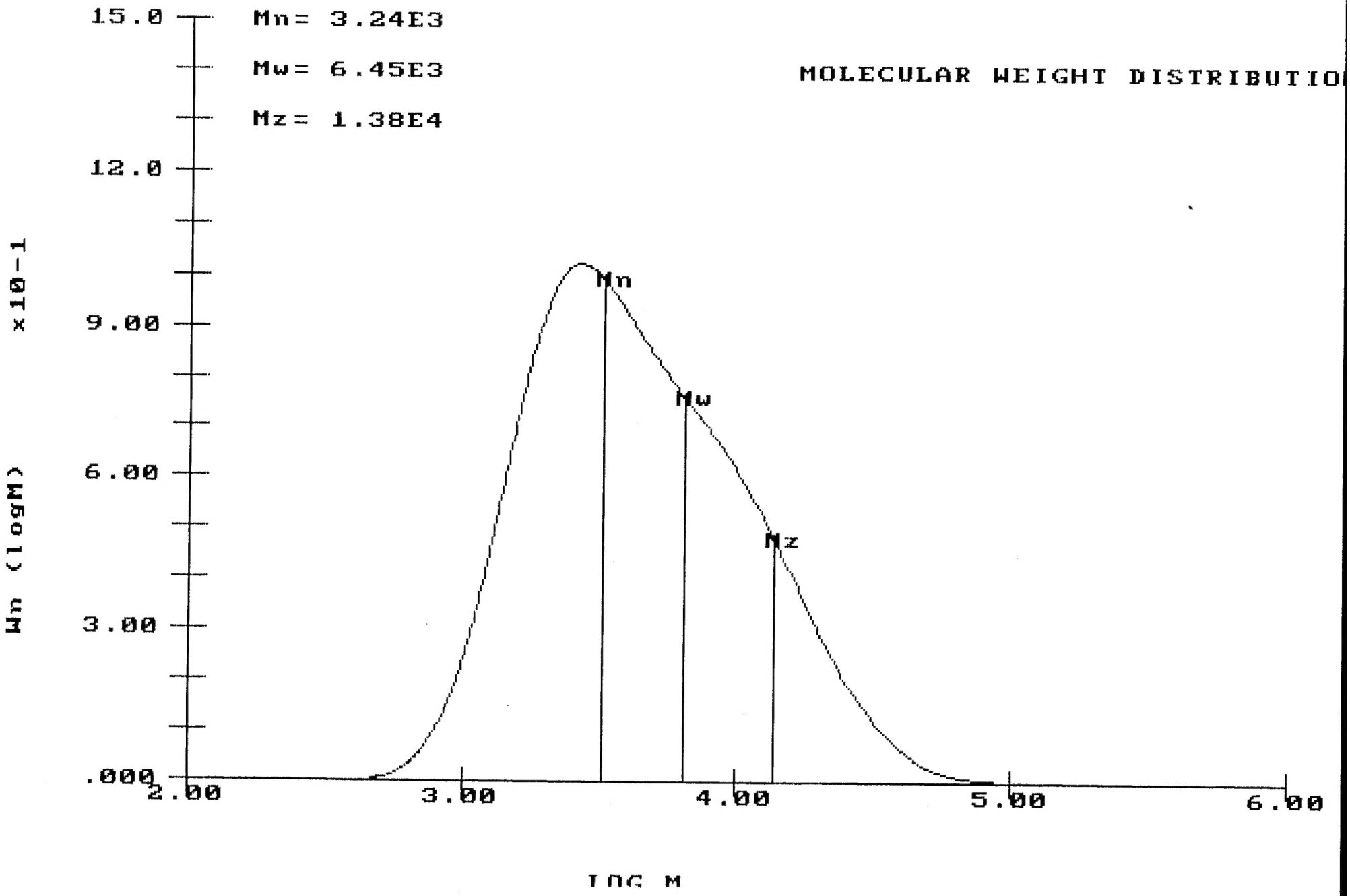

VISCOTEK CORP. UCAL 4.05 ENDED: 06/22/95 10:44

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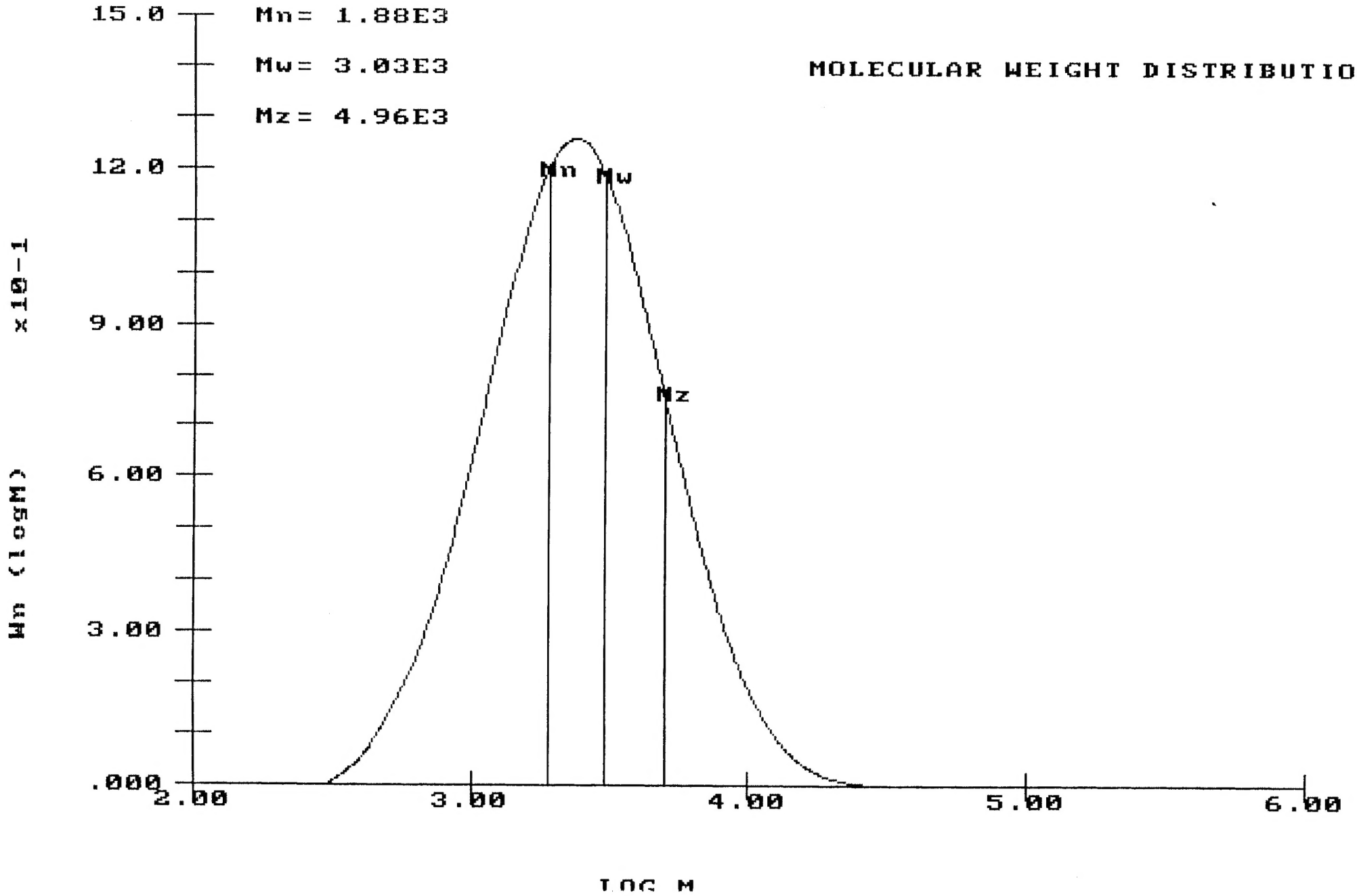

VISCOTEK CORP. UCAL 4.05 ENDED: 10/05/95 15:02

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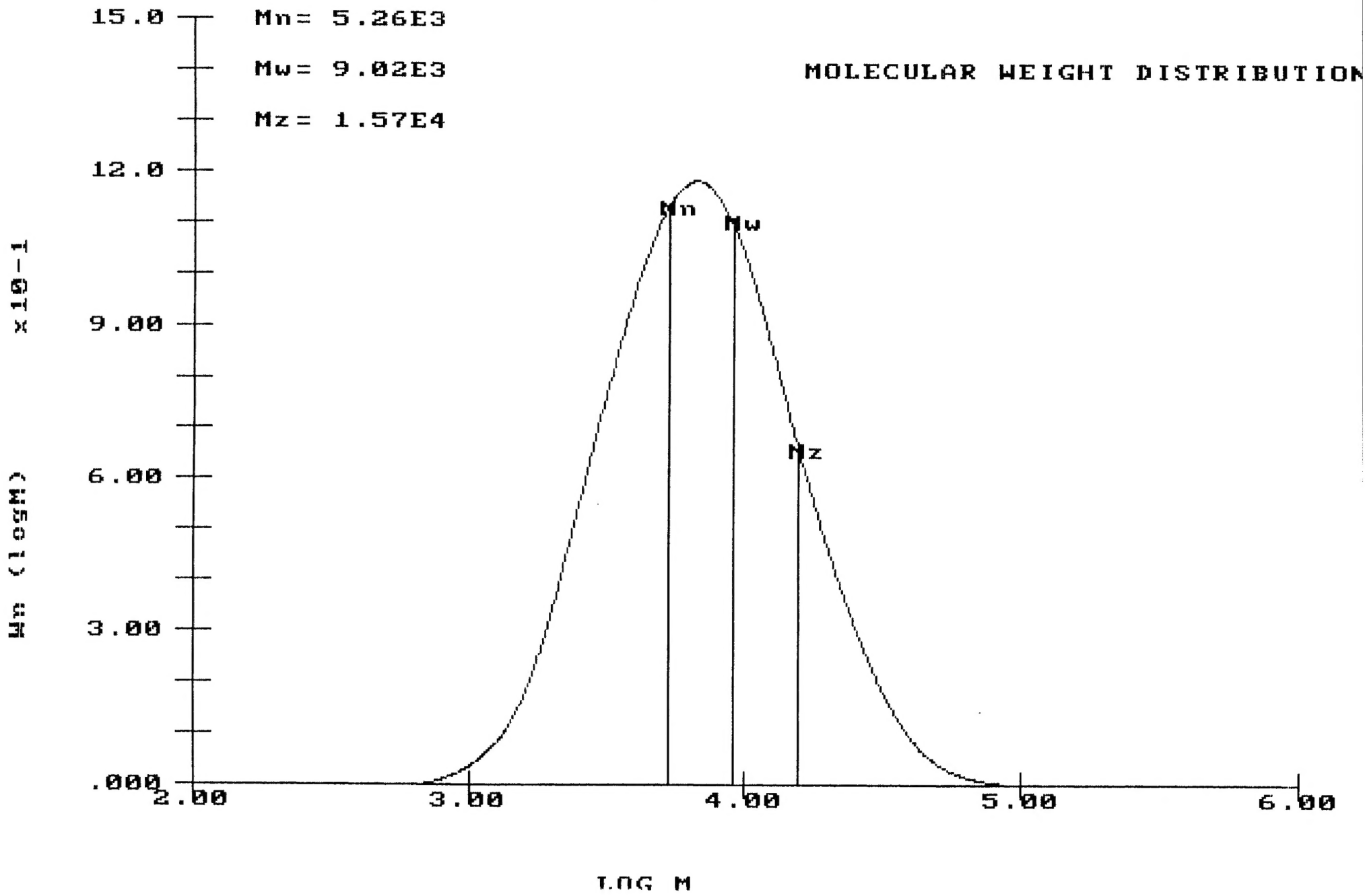

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